No detrimental impact of car manufacturing process and simulation of vehicle in-service conditions on DP1180 hydrogen embrittlement

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SUMMARY

The reduction of the fuel consumption is one major topic for the car makers. One simple way to achieve this issue is to decrease the weight of the vehicles. Therefore the new generation of Advanced High Strength Steels (AHSS) is largely integrated in the modern car bodies. However, the sensitivity to delayed fracture induced by hydrogen is increased for such micro-structures and a tensile strength above 1000 MPa is considered as a potential risky level.
In the present paper, potential impact of carmaking processes like forming, welding, cutting, painting is investigated using hydrogen measurements, carried out by Thermal Desorption Analysis (TDA), and delayed fracture tests performed on small specimens or self stressed welded components more representative of a real part. It is shown that, in the conditions of the tests, no delayed fracture occurs.
In a second stage, the delayed fracture risk due to hydrogen by corrosion is evaluated with a methodology combining various techniques: accelerated corrosion conditions on as delivered or e-coated self stressed components with local damage down to the steel, hydrogen intake evaluation during the corrosion process with TDA. It is demonstrated that, even in detrimental conditions, the most representative configurations, that is to say e-coated and scratched, do not exhibit any delayed cracking.

INTRODUCTION

It is well known that delayed fracture (DF) is due to a critical combination of diffusible hydrogen contained into the material[1,2] and applied or residual mechanical stress for a given metallurgy (figure 1.a). In that case, the hydrogen amount can be introduced during the steelmaking processes (annealing, coating deposit, …) and/or the carmaking processes (welding, phosphating, e-coating, ...). On the other hand, Stress Corrosion Cracking (SCC) refers to a mechanism in which hydrogen is provided by a corrosion attack. In that case, we consider the following realistic situation (figure 1.b): a part made of a potentially sensitive AHSS, with a damaged protective layer and submitted locally to high stresses, which must additionally be exposed to corrosion precisely on this stressed and uncovered area for a time long enough to reach a critical diffusible hydrogen content.

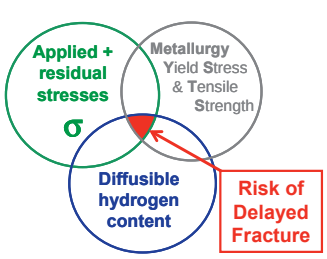

Figure 1a – Delayed Fracture mechanism

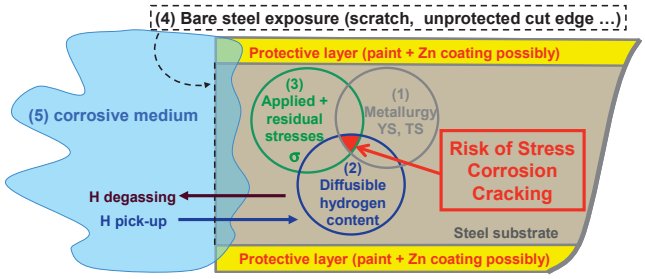

Figure 1b – Additional conditions for Stress Corrosion Cracking

In both cases, one major parameter, regarding the impact of metallurgy, is the tensile stress level of the material. Roughly, the higher the tensile stress the more sensitive to DF or SCC the material will be, leading to the so-called crocodile diagram (figure 2a and b) whose limits diverge usually over 1000 MPa tensile stress.

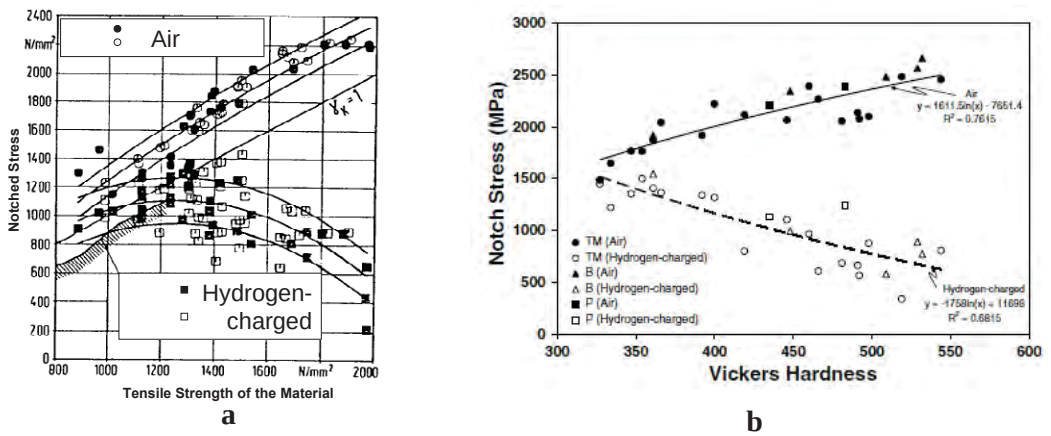

Figure 2a and b – "Crocodile" diagrams starting over 1000 MPa Tensile Stress: a from,[3] b from[4]

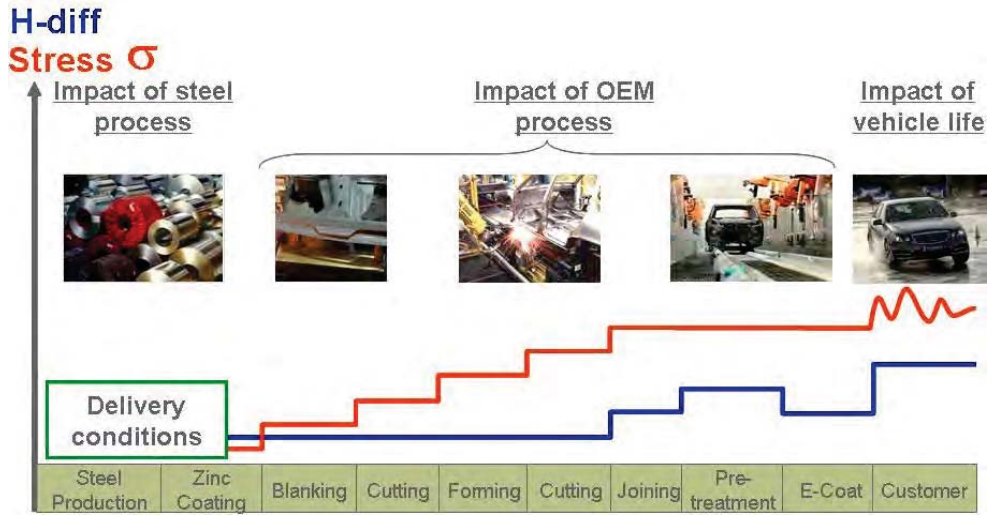

Figure 3 – Schematic hydrogen- and stress levels during carmaking process and vehicle in-service conditions

Within this context, the work reported in this paper aimed at evaluating the real DF and SCC risks linked to the use of a 1200 MPa grade, in particular after the car manufacturing process (DF risk) and during in-service conditions (SCC risk). As shown in figure 3, the detailed objectives are to quantify the hydrogen intake during these steps and to evaluate the potential detrimental impact of an increase of the applied or residual stresses through the testing of realistic (relevant) specimens. Note that, at the delivery state (steelmaker process), the safe use of the material is verified by a constant load tensile test on a punched hole specimen, standardized by the VDA.[5]

MATERIAL

The studied material is a dual phase steel DP1180 whose microstructure and typical mechanical properties are provided in figure 4 and table 1 respectively. Both bare and Electro Galvanized (EG) steels were investigated. As a reference, a zinc coated 1000 MPa grade was also investigated (CP1000 GI).

Table 1 – Mechanical properties of DP1180 (1.5 mm)

Direction	YS (MPa)	TS (MPa)	UEl (%)	TEl (%)
Rolling	980	1191	4.8	8.0
Transverse	1037	1205	5.0	8.9

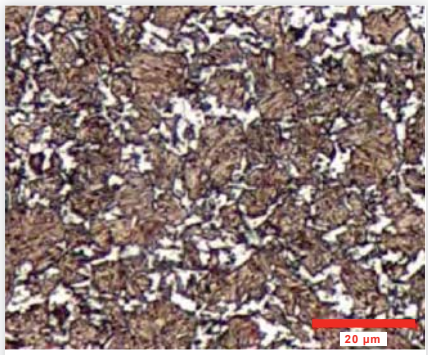

Figure 4 – Microstructure of DP1180 (sodium disulfite etching)

HYDROGEN MEASUREMENT BY TDA

Regarding diffusible hydrogen measurement, an apparatus, which was developed by CRM group, is used at ArcelorMittal R&D. It is a carrier gas method (figure 5a), the sample is heated at a fixed heating rate the H_2 concentration in the N_2 gas is measured by a mass spectrometer (calibration with 50 ppm H_2/N_2 gas). The advantage of this device is a direct measurement on coated material (for instance Zn coated or e-coated). This avoids wrong measurements due to the removal of a coating prior to hydrogen measurements. An example of a measurement on a Zn-coated material is presented in figure 5b. In that case, the heating rate is low in order to allow a good identification of the different desorption peaks (deconvolution), the diffusible hydrogen corresponds to the first peak (content of 0.55 ppm in this example after integration up to 270 °C). Full details about the technique can be found elsewhere.[6]

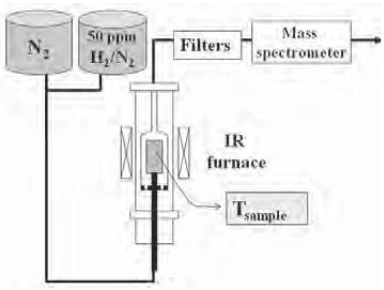

Figure 5a – Synoptic of the TDA used at ArcelorMittal R&D

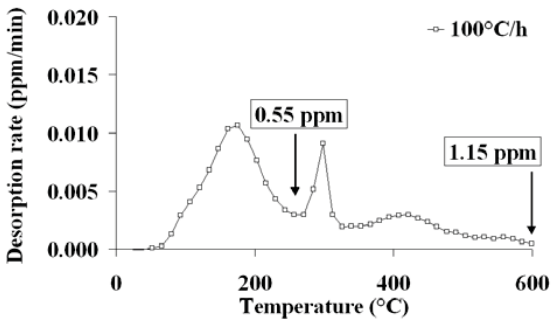

Figure 5b – Example of TDA signal obtained on pre-charged EG coated material (from[3])

IMPACT OF CARMAKER PROCESS

The aim is to quantify hydrogen intake during the carmaker process and assess the delayed fracture risk on a representative component with residual stresses due to forming and welding. This lab component is an over-bent omega shaped rail (to promote residual stresses) closed by a welded plate in order to get the final shape (figure 6). All the elements of the components

Figure 6 – Self-stressed welded component

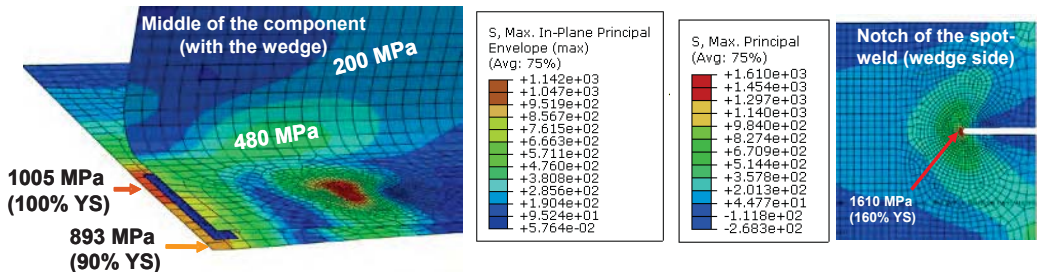

Figure 7 – Finite element simulation to evaluate residual and applied stresses

were basically shear cut. In the middle of the component, a wedge is inserted between the central spot-welds in order to simulate the effect of embossments of a real part (gap effect). It is therefore a self-stressed component (over industrial conditions) with particular high residual stresses on the central spot welds. Finite element simulations have been performed to evaluate local stresses (cut edge and spot weld), cartographies in terms of maximal principal stress are shown in figure 7. As expected, they show high tension areas (red colour) in the spot welds located close to the wedge and in the closure plate which is in contact with the plate.
Tested materials were DP1180 bare, DP1180 EG and CP1000 GI. Some of the components were e-coated or pre-treated as this could be considered as the most critical step regarding potential hydrogen pick up following 2 different processes.

Table 2 – Coating processes investigated

	Degreasing	Pre-treatment	e-coating
Line #1	Alcaline bath (dipping & aspersion)	Zircobond (pH ~ 4.5)	e-coat 20 µm
Line #2	Alcaline bath (dipping & aspersion)	Phosphate (pH ~ 3)	e-coat 20 µm

Small specimens were also processed with the components to measure hydrogen pick up at each step. In order to detect an eventual effect of the forming (dislocations could enhance hydrogen pick up) or the spot welding (local increase of hydrogen due to residual stresses, microstructural heterogeneities, …), 3 types of specimens were used (figure 8): undeformed sheet of 25 x 75 mm as a reference, bent specimen with a 4 mm radius and 2 sheets with two spot welds and an inserted wedge in between.
After one week in a climatic chamber (25 °C, 50 % of relative humidity), no delayed crack was observed on all component configurations. The results of diffusible hydrogen measurements are presented in figure 9. As already explained, TDA were carried out without any removal of coatings (zinc, pre-treatment or e-coat) in order to avoid any artefacts due to this preparation. The pre-treatment (phosphating) of line #2 is more detrimental than the one of line #1 (Zircobond) regarding hydrogen pick up, probably because of the less acidic pH of the Zircobond bath. Concerning the pre-treatment with phosphating, the values are slightly higher on the bent specimen than on the undeformed reference plate. No major effect of the spot welds on the global content is noticed.

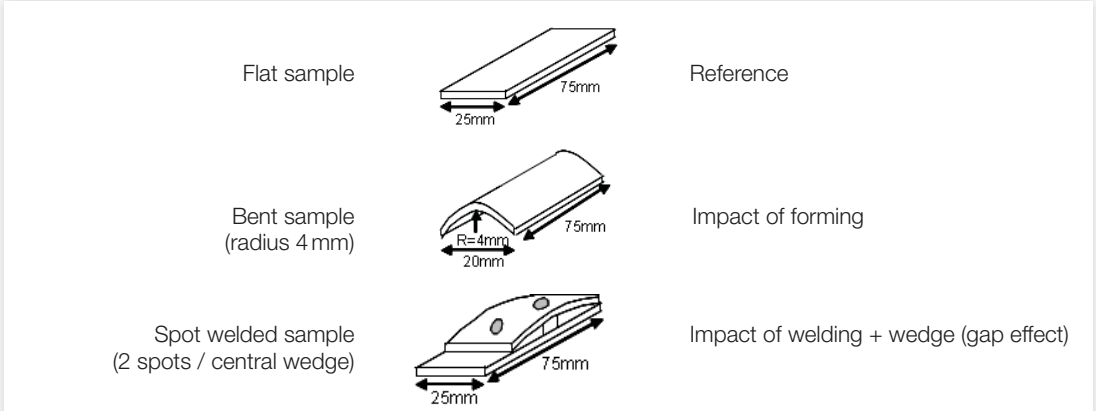

Figure 8 – Specimens for TDA measurements

After e-coating and curing, a degassing is noticed whatever the configuration. The hydrogen content does not exceed 0.1 ppm in any case: most of them are in fact close to 0 ppm, particularly with DP1180 bare and EG results. Actually, the higher residual contents are obtained on the reference CP1000 GI as it is also the most hydrogen charged in its as-delivered state. In any case, all the materials showed no delayed fracture after testing with punch hole specimen tests (SEP1970 procedure [5]), confirming that the level of hydrogen introduced during the most critical stage of the e-coating process (pre-treatment) is not detrimental.

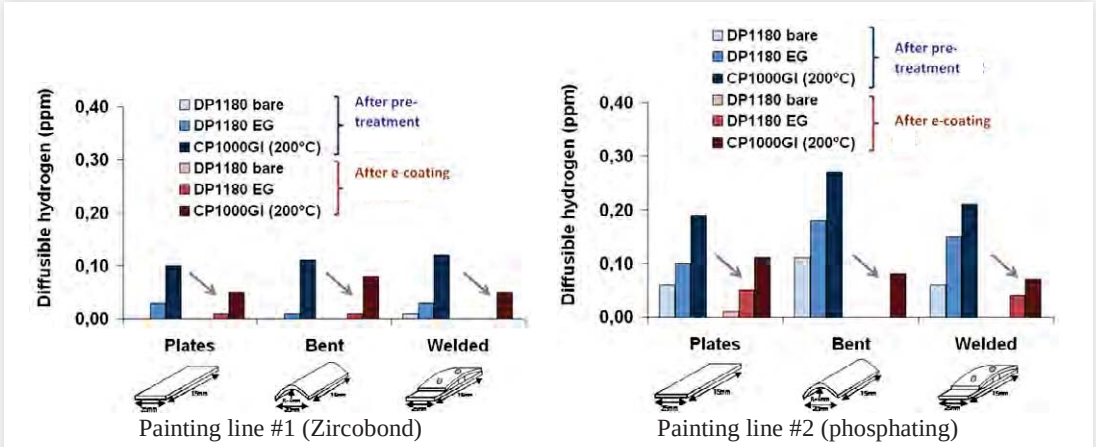

Figure 9 – Hydrogen pick up during e-coating

IN-SERVICE VEHICLE

The aim of this investigation is to evaluate the risk of hydrogen embrittlement due to corrosion. Stress Corrosion Cracking (SCC) tests were launched on the manufactured lab components. Two kinds of corrosion conditions were used: the VDA 233-102 test [7] and an alternating immersion test, proposed and used by Steinbeis Transferzentrum, Korrosion & Korrosionsschutz.

VDA 233-102 TEST:

The VDA 233-102 cyclic corrosion test (figure 10) is considered to provoke accelerated corrosion results representative for a real situation. It combines dry and wet phases and takes temperature variation into account as well.

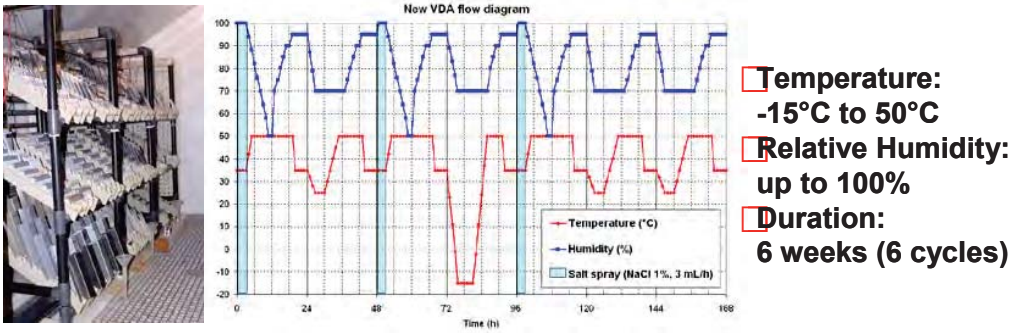

Figure 10 – VDA 233-102 cyclic corrosion test

In order to investigate the impact of corrosion in the most strained areas, 6 weeks of VDA 233-102 were performed on lab components whose e-coat in radii and spotwelds were scratched. On all samples, no SCC was observed (figure 11).

Figure 11 – Lab components with scratches in strained and spot-welded areas, results after 6 weeks of VDA 233-102 cyclic corrosion test

TDA measurements were carried out on both bare and electro galvanized DP1180 after VDA 233-102 cyclic corrosion tests and also Salt Spray Test (SST) to quantify diffusible hydrogen intake. Figure 12 shows the evolution of diffusible hydrogen intake with the 2 kinds of corrosion conditions. There is almost no hydrogen pick up during SST and VDA 233-102 on both bare and DP1180 EG. The hydrogen contents are below 0.1 ppm, in some cases there is also a decreasing trend with time (for instance DP1180 EG in SST). This is consistent with the results of some studies dealing with the quantification of hydrogen entry due to atmospheric corrosion.[8,9]

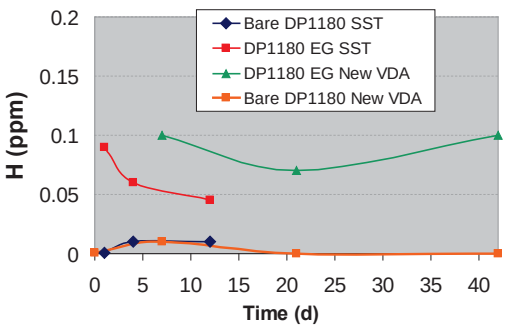

Figure 12 – Diffusible hydrogen pick up during VDA 233-102 and SST

ALTERNATING IMMERSION TEST:

The test has been carried out in a chamber for alternating immersion. It has been modified to apply cyclic mechanical load during the test in order to promote the conditions of crevice corrosion in the area of spot-welds. Therefore additional rigs are installed inside (Figure 13).

With this alternating immersion over 500 h (21 days), the sensitivity against hydrogen inducing damage was investigated on all materials (DP1180 bare, DP1180 EG and CP1000 GI). The specimens were sampled within the lab components (including the 2 spot-welds with the wedge in between). The load was fixed to 3000 N for CP1000 GI and 4500 N for both DP1180 bare and EG in order to get the same global deformation. All materials were tested “e-coated” and “as-welded”. Every three days the specimens were visually inspected for cracks (Table 3):

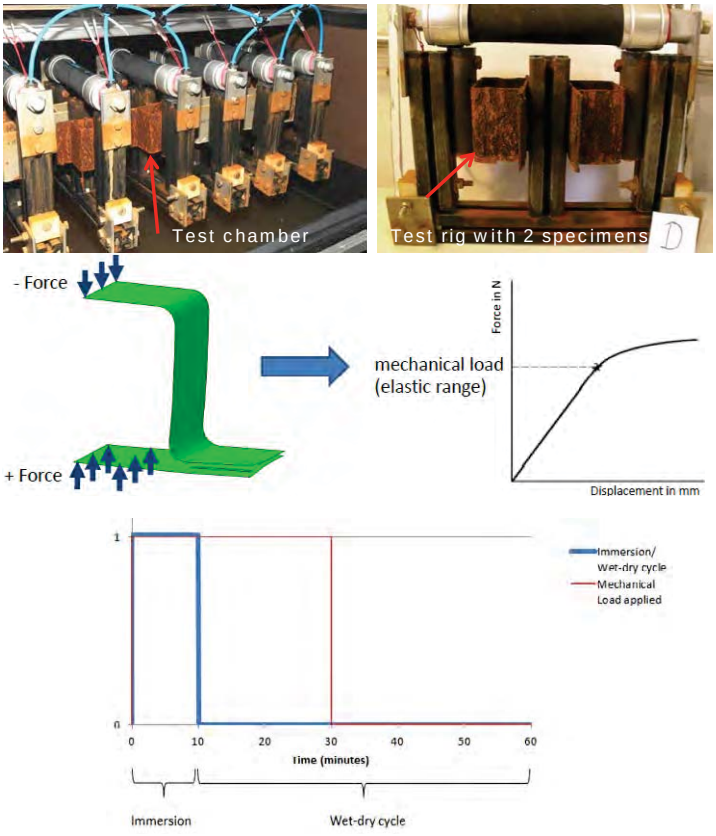

Figure 13 – Alternating immersion test

a) One spot-weld over all DP1180 EG as-welded (uncoated) specimens failed after 500 h (still safe after 432 h) of alternating immersion,
b) No breaks or cracks have been detected on all other specimens (48 spot-welds made of DP1180 among 72)

Table 3 – Synthesis of alternating immersion tests

Time of inspection	504 h	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	x
	432 h	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o
	360 h	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o
	288 h	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o
	216 h	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o
	144 h	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o
	72 h	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o
Specimen		1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
Grade		CP1000 GI			DP1180 bare			DP1180 EG			CP1000 GI			DP1180 bare			DP1180 EG		
State		E-coated									As welded								

x = failure o = non failure

The uncoated lab components are heavily corroded. Complementary metallographic analyses (cross sections) confirm the visual inspection that only one spot failed at 504 h close to the end of the test. Further observation with SEM of the fracture surface points out a brittle area and few typical hydrogen induced damage like cracks between the grain boundaries. However, it cannot be precluded that the fracture is primarily induced by a weld weakness. Particularly in the outer areas of the fracture area, the typical microstructural texture of the material can be detected on the grain boundaries. Additionally the fracture area is remarkably flat along the surface of the sheets (Figure 14).

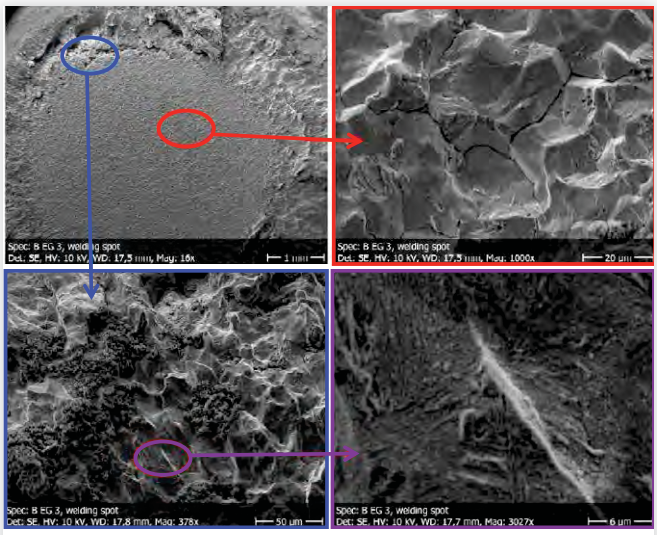

Figure 14 – Fractographic examination of the failed spot-weld

In addition, the residual tensile resistance after exposure to corrosion was measured. All corroded specimens exhibited slightly higher residual tensile forces (statistically better) than the non-corroded ones (as its initial state). The fracture modes resulting from this evaluation of residual tensile resistance do not differ as plug failures are observed in all cases, except for the sole failed spot-weld. Figure 15 provides the picture of plug failure of remaining DP1180 EG specimens in as-welded condition after 504 h of

alternating immersion in comparison with the initial state. Summarizing, no hydrogen-induced damage after exposure to corrosion in the alternating immersion test is detectable by a reduction of the tensile resistance or a modification of the failure modes. Therefore, the hypothesis of a failure during corrosion exposure due to a hydrogen induced damage mechanism is rather doubtful. It is assumed that the failure is more linked to an initial defect of the spot-weld.

Initial state | **Specimen #1 after 504 hours** | **Specimen #2 after 504 hours**

Figure 15 – Residual tensile resistance and plug failure mode of DP1180 EG as-welded spots before (initial state) and after alternating immersion tests

CONCLUSION

A new method to assess most realistic delayed fracture and stress corrosion cracking risks was proposed. It is based on the testing of lab components which aims to be as most representative of real parts life (over the industrial constraints). The methodology was applied to a 1200 MPa grade (DP1180) which could be considered as a possibly risky level.

The main output are:

- The hydrogen pick up during the manufacturing process e-coating is low (two processes tested). After curing, the final contents are possibly lower than the initial ones. The non-detrimental impact of this carmaker process is confirmed by the resistance to severe delayed fracture tests on small specimens.
- The e-coated and scratched self-stressed lab components do not exhibit any delayed crack after cyclic corrosion tests (VDA 233-102). Hydrogen measurements on samples which were corroded in the same conditions showed, that diffusible hydrogen pick up remains low despite this corrosion attack.
- Pieces sampled from lab components (including the wedge insertion) were also tested by combining applied load and corrosion (alternating corrosion tests). Among 72 spot-welds, only one failed on EG, uncoated material. However, destructive tensile test carried out after corrosion exposure do not point out any global hydrogen induced damage. The most probable hypothesis is an initial defect of this spot-weld.

With respect to body-in-white applications with similar conditions to this study, no hydrogen cracking should be observed.

REFERENCES

[1] Evaluation method for delayed fracture susceptibility of steels and development of High strength Steels with high Delayed Fracture resistance. S. Yamasaki, M. Kubota, T. Tarui. Nippon Steel Technical report n° 80 July 1999

[2] Evaluation methods of hydrogen embrittlement for ultra-high strength steel sheets for automobiles. S. Takagi, Y. Toji, K. Hasegawa, Y. Tanaka, N. Rössler , B. Hammer, T. Heller. Material Science and Technology, October 2010 Houston

[3] Einfluss unterschiedlicher Wärmebehandlungsverfahren auf die wasserstoffinduzierte Sprödbruchbildung bei Vergütungsstählen für die Schraubenfertigung. K.H. Kloos, R. Landgrebe, H.Speckhardt. Z.Werkstofftech. 18, 411-422 (1987)

[4] Role of microstructure, composition and hardness in resisting hydrogen embrittlement of fastener grade steels. N. Nanninga, J. Grochowsi, L. Heldt, K. Rundman. Corrosion Science 52 (2010) 1237-1246

[5] Test of the resistance of Advanced High Strength Steels (AHSS) for automotive applications against production related hydrogen induced brittle fracture. SEP1970, September 2011, 1st edition

[6] Determination of diffusible hydrogen content in coated High Strength Steels. C. Georges, T. Sturel. Proceedings of the Hydrogen International Conference 2008

[7] F. Beier, K-H. Stellnberger, S. Geisler, A new accelerated cyclic corrosion test for automotive substrates, EUROCORR Congress September 2009, Nice France,

[8] Hydrogen Entry into Steel by Atmospheric Corrosion. T.Kushida, ISIJ International, Vol. 43 (2003), No. 4, pp. 470-474

[9] Evaluation of delayed fracture property of outdoor-exposed high strength AISI 4135 steels. S. Li, E. Akiyama, N. Uno, K. Hirai, K. Tsuzaki, B. Zhang, Corrosion Science, 52 (2010), pp. 3198-3204.